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PYROSULPHURYL CHLORIDE AND CHLORSULPHONIC ACID.

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During certain investigations in this laboratory it became necessary to find better methods for the separation and purification of pyrosulphuryl chloride and chlorsulphonic acid than heretofore described, and to determine with greater accuracy their more important physical constants. It was very soon evident, not only that much of the literature on the subject was valueless, since most observers had worked with a mixture of the two substances or with impure material, but also that a separation of the mixture into pure components or a complete purification of either body could not be readily accomplished on the lines laid down by these observers. We have succeeded, however, by utilizing some of the facts already known and others which became evident in the course of our investigation, in preparing both of these bodies in quantity and of great purity.[1]

Historical.

Action of Metallic Chlorides on Sulphur Trioxide.

The complete history of pyrosulphuryl chloride and chlorsulphonic acid begins in 1822–1823 with the study of the reaction between sulphur trioxide and sodic chloride at high temperature by Sertürner,[2] Döbereiner,[3] and Gmelin.[4] Sertürner had erroneously considered the products to be hydrochloric acid and sodic sulphate; Döbereiner thought that a gaseous compound of chlorine and sulphur dioxide was formed, while Gmelin showed, although only qualitatively, that the gaseous product was a mixture of chlorine and sulphur dioxide. Rose[5] in 1836 investigated the reaction at low temperature, using other metallic chlorides as well. Fused sodic chloride absorbed anhydrous sulphur trioxide, forming a solid, transparent mass, which, when heated, gave chlorine and sulphur dioxide, similarly to Gmelin's observation. Undoubtedly, as R. Williamson[14] also points out, Rose had in his hands the sodium salt of chlorsulphonic acid. Rosenstiehl[6] in 1861 distils a mixture of fused

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[1] Acknowledgment is due to Mr. Laurence Haines Whitney for much assistance in the beginning of this investigation, particularly in the separation of pyrosulphuryl chloride and chlorsulphonic acid by crystallization and centrifugal filtration at low temperature, and in the study of the use of phosphorus pentoxide as a dehydrating agent, both in the preparation of the two bodies and in the conversion of chlorsulphonic acid to pyrosulphuryl chloride.

[2] Gilbert's Ann., **72**, 109 (1822).

[3] Ibid., **72**, 331 (1822).

[4] Ibid., **73**, 209 (1823).

[5] Pogg. Ann., **38**, 117 (1836).

[6] Compt. rend., **53**, 658 (1861); Jahresb., 1861, 120; Rep. chim. pur., **4**, 60 (1861).

sodic chloride and excess of sulphur trioxide until the retort contents were completely melted. On rectifying the distillate over fused sodic chloride, he obtained a liquid boiling at 145–150°; specific gravity, 1.762; vapor density, 3.76 (referred to air), which he considered from the analysis to be pyrosulphuryl chloride. These properties, however, together with the fact that it reacted violently with water, show a considerable admixture of chlorsulphonic acid. This is apparently the only source of the statement one finds in the literature that pyrosulphuryl chloride is formed by heating sodic chloride with sulphur trioxide.[7]

Action of Non-metallic Chlorides on Sulphur Trioxide.

Rose[8] in 1838 passed the vapor of anhydrous sulphur trioxide through sulphur monochloride at low temperature. On fractioning the product, an oily liquid of specific gravity 1.818 at 15° was obtained, boiling at 145°, which was slowly decomposed with water. This was the first preparation of pyrosulphuryl chloride, but it undoubtedly contained chlorsulphonic acid which is invariably formed whenever sulphur trioxide is chlorinated in the presence of even a small amount of water (*v.* Table II), and there may have been some sulphur monochloride present, since the boiling point of the latter, 138°, is so near that of the main product. By using phosphorus trichloride Rose obtained a similar liquid, boiling between 137° and 165°, containing much phosphorus. In 1839 Rose,[9] with the idea of preparing sulphuryl chloride, discovered in the same year by Regnault,[10] mixed fused sodic chloride with "pure" pyrosulphuryl chloride, probably prepared by a modification[11] of his original method, in which he distilled sulphur monochloride with ordinary fuming sulphuric acid. A solid mass was formed, resembling that which he had previously obtained[5] by the action of sodic chloride on sulphur trioxide. Distillation gave chlorine, sulphur dioxide, and a liquid boiling at 145°, which he concludes to be pure, undecomposed pyrosulphuryl chloride. From consideration of our work, the result is clear. There was much chlorsulphonic acid in the supposed "pure" pyrosulphuryl chloride, and this was converted to its sodium salt, from which the unchanged pyrosulphuryl chloride was distilled. If Rose

[7] E. g., Roscoe and Schorlemmer, Treatise on Chemistry, I, 438 (1905); Dammer, Handbuch, I, 667 (1892).

[8] Ann. d. Phys. u. Chem., **44**, 291 (1838); Berzelius Jahresb., **19**, 201 (1840); Gmelin, Handbuch, I, 778.

[9] Pogg. Ann., **46**, 167 (1839).

[10] Compt. rend., **7**, 895 (1838).

[11] Pogg. Ann., **46**, 177 (1839).

had known that this was a process of rectification, we might have had pure pyrosulphuryl chloride at an earlier date. The further researches of Rose [12] do not throw any light on the preparation of either body.

A. Williamson [13] in 1854, by the action of phosphorus pentachloride on "sulphuric acid" (strength not stated), obtained a liquid boiling at 145°, decomposing violently with a small amount of water, quietly with an excess. No method of purification is given, nor are there any analyses of the product, but Williamson concludes that it was chlorsulphonic acid, and advances for the first time the theory of the successive substitution of the hydroxyls in sulphuric acid by chlorine. He makes a crude sodium salt, and considers the acid itself to be identical with the preparation of Rose,[8] for in his opinion that contained "the elements of water." Williamson obtains a "similar" acid by the action of hydrochloric acid on sulphur trioxide, which must be taken as the first use of this reaction in the preparation of chlorsulphonic acid. Though both of his products were impure, the first probably contained some pyrosulphuryl chloride, the second none.

R. Williamson [14] in 1857 states that chlorsulphonic acid can be made by the action of chloride of sulphur and chlorine on sulphuric acid and by the combination of chlorine and sulphur dioxide in contact with heated platinum black. The product of the first reaction is said to have the same properties as that obtained by A. Williamson, but details of purification, properties, and methods of analysis are lacking. From information supplied by A. Williamson, it is stated that continued distillation of the body leads to its decomposition into sulphuric acid and sulphuryl chloride.

Schiff [15] in 1857 shows that the supposed compound of phosphorus pentachloride and sulphur trioxide obtained by Persoz and Bloch [16] was identical with the preparation of A. Williamson, and obtained by the reaction a liquid boiling at 140–150°, which decomposed with water into sulphuric and hydrochloric acids.

Baumstark [17] in 1866, using phosphorus pentachloride with fuming sulphuric acid, obtained a liquid boiling from 145° to 156°, mainly at 150–152°, decomposing gradually with much water, violently with a small amount. The agreement of the vapor density (4.10) with the

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[12] Pogg. Ann., **52**, 57 (1841); **85**, 510 (1852).

[13] Proc. Roy. Soc., **7**, 11 (1854); Phil. Mag. (4), **7**, 365 (1854); Jour. Chem. Soc., **7**, 180 (1855); Jour. prakt. Chem., **62**, 377 (1854); Ann., **92**, 242 (1854).

[14] Jour. Chem. Soc., **10**, 97 (1858); Jour. prakt. Chem., **73**, 73 (1858).

[15] Ann., **102**, 114 (1857).

[16] Compt. rend., **28**, 86 (1849).

[17] Ann., **140**, 75 (1866).

calculated (4.03) and the analysis indicated a pure chlorsulphonic acid, but there was probably enough pyrosulphuryl chloride present to raise the low density which pure chlorsulphonic acid usually shows owing to its dissociation. Similarly, Williams [18] in 1869, repeating the Williamson reaction in the latter's laboratory, is led by density (4.56) and analyses to consider his product pure chlorsulphonic acid. The boiling point is not given.

The first recorded use of carbon tetrachloride as a chlorinating agent is by Schützenberger [19] in 1869. On warming this with sulphur trioxide until the phosgene was expelled, a product was obtained boiling at 130°, reacting "at once" with water, and giving "figures leading to the formula $S_2O_5Cl_2$." The sulphur trioxide was evidently hydrated and the product contained much chlorsulphonic acid. In the next year Armstrong [20] repeated the reaction and suggested its use as a source of phosgene. His product boiled between 141° and 145°, was difficult to purify, and did not decompose water easily. The analysis corresponded more nearly to that of pyrosulphuryl chloride. Substituting chloroform for carbon tetrachloride, Armstrong obtains what he considers from the analysis to be a mixture of the two bodies. He also investigates the action of phosphorus trichloride on sulphur trioxide, but with unsatisfactory results.

Prudhomme [21] in 1870 tried the action of hexachlorethane on sulphur trioxide in a closed tube at 150°. The product boiled at 140° and was considered to be pyrosulphuryl chloride. No analytical data are given.

The study of the question by Michaelis [22] in 1871 and succeeding years is of interest. Using sulphur trioxide "free from hydrate" with phosphorus pentachloride he obtains "pyrosulphuryl chloride" according to the reaction :

$$2SO_3 + PCl_5 = S_2O_5Cl_2 + POCl_3.$$

The product boiled at 143°, acted quietly with water, and had a specific gravity of 1.819 at 18°. With sulphuric acid, the reaction was considered to be

$$3H_2SO_4 + PCl_5 = 3SO_3HCl + HPO_3 + 2HCl$$

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[18] Jour. Chem. Soc., **22**, 304 (1869); Zeitschr. f. Chem., **12**, 665 (1869).
[19] Compt. rend., **69**, 352 (1869); Jahresb., 1869, 209; Ann., **154**, 375.
[20] J. prakt. Chem., **109**, 244 (1870); Ber., **2**, 712 (1869) and **3**, 730 (1870).
[21] Compt. rend., **70**, 1137 (1870); Ann. Chem. Pharm., **156**, 342 (1870).
[22] Jena Zeitschr., **6**, 235 (1871); Zeitschr. f. Chem. (2), **7**, 149 (1871).

and the product "pure" chlorsulphonic acid. It boiled at 158.4° and had a specific gravity of 1.776 at 18°. No sulphuryl chloride was formed by the action of phosphorus pentachloride on either sulphur trioxide or chlorsulphonic acid, as Williamson [13] and Schiff [15] had stated, nor, according to Odling [23], by treating plumbic sulphate with phosphorus oxychloride. While Michaelis did not obtain pure products, he at least brought out the association of the two bodies in the chlorination product, and his results show the influence of hydration of the sulphur trioxide. In another paper, [24] in 1871, he obtains chlorsulphonic acid from sulphuryl chloride and water and from sulphuryl chloride and sulphuric acid. The Carius [25] reaction of phosphorus pentachloride on plumbic sulphate gave neither body. In a third paper [26] in 1873 he makes chlorsulphonic acid from concentrated sulphuric acid and phosphorus trichloride in a current of chlorine. Geuther [27] had tried this without chlorine.

Müller [28] in 1873 prepares "chlorsulphonic acid" with phosphorus pentachloride and "moderately fuming" sulphuric acid. He also distils a mixture of fuming sulphuric acid and phosphorus pentoxide in a current of hydrochloric acid gas, and considers the product identical with that made by the action of hydrochloric acid on sulphur trioxide. There are no data by which the quality of these preparations may be judged, and they were probably quite impure. Clausnizer [29] in 1878 prepares chlorsulphonic acid according to Michaelis by action of phosphorus trichloride on sulphuric acid in a current of chlorine, obtaining a boiling point of 150–151° at 726 mm. Thorpe [30] in 1880 uses the Rose reaction with sulphur monochloride to prepare "pyrosulphuryl chloride," which boils at 139.59°, corr., with specific gravity 1.85846 at 0° referred to water at 4°. By action of phosphorus oxychloride on "the strongest oil of vitriol," he prepares "chlorsulphonic acid," boiling at 155.3°, corr., with specific gravity of 1.78474. He finds that chlorsulphonic acid is completely converted to sulphuryl chloride and sulphuric acid by heating for some hours at 200°.

Ogier [31] in 1882, during a thermochemical study of the oxychlorides of sulphur, prepared pyrosulphuryl chloride by the first method of Rose; the product boiling at 140.5° and reacting quietly with water. A preparation of "chlorsulphonic acid" by the Armstrong reaction of sulphur trioxide and chloroform showed violent action with water. No

[23] Gmelin, Handbuch, **1**, 169.
[24] Jena Zeitschr., **6**, 293 (1871).
[25] Ann., **106**, 307 (1858).
[26] Ibid., **170**, 1 (1873).
[27] Ber., **5**, 924 (1872).
[28] Ibid., **6**, 227 (1873).
[29] Ibid., **11**, 2007 (1878).
[30] J. Chem. Soc., **37**, 358 (1880).
[31] Compt. rend., **94**, 82 (1882).

boiling point is given for this product, and Armstrong's opinion is overlooked, that the reaction gives a mixture of the two bodies. In a second paper [32] Ogier determines the vapor density of what was probably the same or a similar preparation of pyrosulphuryl chloride. As his analyses convinced him of the purity of his product, the deviation of the density (3.70) from the theoretical (7.49), together with his inability to synthesize pyrosulphuryl chloride from sulphur trioxide and sulphuryl chloride, causes him to find here an exception to Avogadro's Rule!

In contrast to the previous confusion, the work of Konovaloff [33] in 1882 is clear. This author prepared pyrosulphuryl chloride by the method of Schützenberger,[19] using twice distilled sulphur trioxide, in which, however, the actual amount of moisture was not determined. During the reaction and subsequent distillation, moisture was excluded and connections were of glass. The product boiled at 153° (752 mm.); another preparation at 152.5° (740 mm.). The specific gravity was 1.872 at 0°. Water acted slowly. The analyses were good, and the vapor density (in aniline, 7.31; in nitrobenzene, 7.27) showed that Avogadro's Rule was not in immediate danger of overthrow. Konovaloff notes that the boiling point of his product was much higher than that of previous observers, notably that of Ogier, and considers that previous preparations may have been contaminated with chlorsulphonic acid, which dissociates easily. On mixing equal parts of his product with chlorsulphonic acid prepared by the Williamson [13] method, a boiling point of 140–146° was obtained, with vapor density of 4.10 at 210°. From four parts of water and one hundred parts of his product, he obtained a liquid boiling at 139–140°, with vapor density of 4.07. Ogier,[34] in reply, admitted the possibility of a small amount of chlorsulphonic acid in his product, but not enough to lower the vapor density to 3.70.

Heumann and Köchlin [35] in 1883 were unable to synthesize pyrosulphuryl chloride from sulphur trioxide and sulphuryl chloride. Using the method of Rose,[8] they obtained a product which they did not think could contain chlorsulphonic acid, since it was "unchanged" by distillation with phosphorus pentoxide. Yet it boiled at 145–147°, with vapor densities from 5.84 in aniline to 2.58 in sulphur, and gave inconclusive figures on analysis. They think that dissociation of pyrosulphuryl chloride takes place into sulphur trioxide, sulphur dioxide, and chlorine, and is nearly complete at the boiling point of sulphur.

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[32] Compt. rend., **94**, 217 (1882).
[33] Ibid., **95**, 1284 (1882).
[34] Ibid., **96**, 66 (1883).
[35] Ber., **16**, 479 (1883).

Possibly the work of Konovaloff had escaped their observation. Later in another paper,[36] from the vapor density at 184°, they decide that chlorsulphonic acid (2 vols.) at that temperature is completely dissociated into sulphur trioxide, sulphur dioxide, chlorine, and water (8 vols.).

Konovaloff[37] in 1883, applying again his entirely correct theory of the necessity for anhydrous reagents, obtained through the Rose reaction with sulphur monochloride a pyrosulphuryl chloride boiling at 152–153°, with vapor density of 7.2 at 210°.

Since 1883, little more concerning the chlorination methods has been published. Erdmann[38] in 1893, as did Armstrong earlier, proposes the reaction of Schützenberger,[19] with slight modifications, as an economical method for preparing phosgene. The residue he considers a mixture of pyrosulphuryl chloride and chlorsulphonic acid. Moureau[39] in 1894, by the action of thionyl chloride on sulphuric acid of specific gravity 1.84, obtains a product boiling at 130–157°, which he concludes to be a mixture of the two bodies. Prandtl and Borinski[49] have used the method of Schützenberger in the investigation cited below, and show that both bodies are present in the reaction product.

Action of Hydrochloric Acid on Sulphur Trioxide.

As previously mentioned, A. Williamson,[13] in 1854 was apparently the first to use this reaction, of which chlorsulphonic acid and not pyrosulphuryl chloride is the product. The reaction was repeated in 1857 in A. Williamson's laboratory by R. Williamson,[14] but no details are given. Dewar and Cranston[40] in 1869, also, by the "direct action of sulphuric acid on hydrochloric acid," obtain a substance "with all the properties ascribed by Williamson."

Much more definite is the work of Beckurts and Otto[41] in 1878, who advised the use of a fuming sulphuric acid, slightly crystalline at ordinary temperature, "containing from 38 to 39 per cent of sulphur trioxide."[42] Their product boiled between 149° and 152.7°, mainly at 151.7–152.7°, and was apparently fairly pure. Beckurts and Otto consider that, if chlorsulphonic acid and sulphuric acid give pyrosul-

[36] Ber., **16**, 602 (1883).
[37] Compt. rend., **96**, 1146 (1883).
[38] Ber., **26**, 1990 (1893).
[39] Bull. Soc. Chim. (3), **11**, 767 (1894).
[40] Chem. News, **20**, 174 (1869).
[41] Ber., **11**, 2058 (1878).
[42] This would mean about 94 per cent actual sulphur trioxide, or about 66 per cent available (*v.* Table II, p. 687).

phuric acid and hydrochloric acid, according to Williams,[18] the formation of chlorsulphonic acid by their method must be due to the concentration of the hydrochloric acid, i. e.,

$$H_2S_2O_7 + HCl \rightleftarrows H_2SO_4 + SO_3HCl.$$

Though Müller[28] in 1873 had added phosphorus pentoxide to the fuming acid, presumably to increase the yield, it is not clear that he understood the action of the hydrochloric acid to be on the free sulphur trioxide only. Beckurts and Otto could not substantiate the result of A. Williamson,[43] furthur studied by Behrend[44] and later proved by Ruff,[45] that chlorsulphonic acid, heated to 170–180°, gives sulphuric acid and sulphuryl chloride, for they considered that sulphur dioxide and chlorine were the primary products; sulphuryl chloride a secondary one.

Nothing new in regard to this method has apparently been published in the past thirty years. We find further no specific statement of its use in the preparation of material for investigation. Though it has undoubtedly been employed, yet most of the preparations of chlorsulphonic acid, so called, seem to have been made with non-metallic chlorides.[46]

The contribution of Ruff[45] in 1901 to the knowledge of chlorsulphonic acid is important, and throws light on the somewhat discordant observations of former investigators. He does not state the method of preparation, but this is of no importance to his paper. He studies the decomposition to sulphuryl chloride and sulphuric acid by means of catalysers, and bases on this study a valuable technical method for the preparation of sulphuryl chloride. In Ruff's opinion, no chlorine or sulphur dioxide is formed at the boiling point, nor between 170° and 180°, but only at higher temperatures.

The Relation of Pyrosulphuryl Chloride and Chlorsulphonic Acid to Each Other; their Separation and Purification.

The simultaneous formation of pyrosulphuryl chloride and chlorsulphonic acid by the action of chlorides on a hydrated sulphur trioxide, though noted by some observers, does not receive serious consideration until taken up by Konovaloff, who showed that the dehydration of chlorsulphonic acid by phosphorus pentoxide was only partial,[37] but

[43] Quoted by R. Williamson (note 14, p. 676).
[44] Ber., **8**, 1004 (1875).
[45] Ibid., **34**, 3509 (1901).
[46] E. g., Besson (note 48, p. 682).

was able to convert pyrosulphuryl chloride to chlorsulphonic acid by addition of water.[33] Heumann and Köchlin[35] did not think that there was any dehydration of chlorsulphonic acid by phosphorus pentoxide.

Billitz and Heumann[47] in 1883 heated chlorsulphonic acid (method of preparation and properties not given) with nearly equal weight of phosphorus pentoxide. The product, redistilled over phosphorus pentoxide, boiled at 145–147° at 724 mm., and the analysis was close to the theory for pyrosulphuryl chloride. The vapor density was 5.89, with evidence of decomposition. Clearly the dehydration was only partial. Conversely, by adding 3 grams of water to 40 grams of pyrosulphuryl chloride, the product boiled at 154–158° at 723 mm., reacted violently with water, and gave an analysis corresponding more nearly to chlorsulphonic acid.

Besson[48] in 1897 studied the purification of the two bodies, but the method of preparation, vapor density, specific gravity, and analyses of his crude products are not given. Crude pyrosulphuryl chloride contained chlorsulphonic acid, chlorine, sulphur dioxide, and sulphur trioxide, and could not be distilled at ordinary pressure without decomposition into the last three. Mercury at low temperature removed the free chlorine; at 60° took the chlorine from the compound, setting free sulphur dioxide and trioxide. At 100° in a closed tube, sulphur dioxide was the only gaseous product, mercuric sulphate and chloride being formed. Most of these decomposition phenomena may of course be ascribed to the chlorsulphonic acid present. By using phosphorus pentachloride, Besson thought to remove the sulphur trioxide and to dehydrate the chlorsulphonic acid in his crude pyrosulphuryl chloride, but his product boiled at 142–143° (765 mm.). Apparently, distillation at 15 mm. gave what he considered pure products; pyrosulphuryl chloride boiling at 53°, chlorsulphonic acid at 65°. The former gave white crystals at — 39°; the latter did not solidify at — 75°. The boiling point of chlorsulphonic acid at 765 mm. was 152°. Besson could not cause sulphuryl chloride and sulphur trioxide to unite either in sunlight or at 100°.

During the preparation of this paper, the completion of which has been unavoidably delayed, Prandtl and Borinski[49] have proposed a method for the preparation of pure pyrosulphuryl chloride which depends on the destruction of the chlorsulphonic acid in the mixture formed in the Schützenberger reaction. The method is considered by them to obviate the necessity for use of anhydrous material and ex-

[47] Ber., **16**, 483 (1883). [48] Compt. rend., **124**, 401 (1897).
[49] Zeitschr. anorg. Chem., **62**, 24 (1909).

clusion of moisture in carrying out the reaction, as recommended by Konovaloff. It was clear to them, from the color reactions with tellurium and selenium, as well as from analyses of the fractions, that the two bodies were both present and could not be separated by fractionation. On the assumption that chlorsulphonic acid is more readily attacked by water than pyrosulphuryl chloride, they treat the crude distillate with ice in a freezing mixture. The lower layer of pyrosulphuryl chloride is separated from the upper of sulphuric acid, and distilled, with or without phosphorus pentoxide. Seventy per cent of the crude pyrosulphuryl chloride was recovered, boiling at 150° (720 mm.). The analysis gave almost theoretical figures, and the specific gravity was 1.876 at 0°; 1.844 at 18°. Vapor density determinations by the Meyer method gave 7.15 and 7.27 (theory, 7.49). In making these, the bulb of the apparatus was heated with phosphorus pentoxide before adding the substance. Other trials, without this desiccation, gave 5.94 and 6.32.

Prandtl and Borinski find the action of tellurium and selenium useful in distinguishing between the two bodies. Chlorsulphonic acid gives with the first a cherry red color, with the second a dark green, while pyrosulphuryl chloride gives no color with either. They consider that pyrosulphuryl chloride is not converted to chlorsulphonic acid by water, but directly to sulphuric and hydrochloric acids. Adding five grams of water to sixty grams of pyrosulphuryl chloride (equal molecules) they obtain sulphuric acid and a distillate boiling at 140–147°, which they consider to be unaltered substance, since it dissolved in water slowly and was not colored by tellurium.

Historical Summary.

The table on the following two pages shows briefly the results obtained by former investigators:

The Results of this Investigation.

It is clear, from consideration of the foregoing and from our own work, that the most reliable preparations of pyrosulphuryl chloride were those of Konovaloff and of Prandtl and Borinski, while Beckurts and Otto have described the only reasonably pure preparation of chlorsulphonic acid. It is evident, also, that while either body, with proper precautions, may be prepared without a large admixture of the other, or of the decomposition products of either, yet it is somewhat doubtful whether an absolutely pure preparation of either has been made, especially in large quantities. Further, the widely differ-

TABLE I.

RESULTS OF PREVIOUS INVESTIGATORS.

Reference Numbers.	Investigator.	Specific Gravity.	Vapor Density (air).	Boiling Point C°.	Action with Water.	State of SO_3.	Reagent used.	Probable Prepond-erating Body.
6	Rosenstiehl	1.762	3.76	145–150	Rapid	Solid	NaCl	C
8	Rose	1.818 (15°)	...	145	Slow	Vapor	S_2Cl_2	P
8	Rose	....	...	137–165	...	Vapor	PCl_3	P
9	Rose	....	...	145	...	Fuming sulph. acid	S_2Cl_2	P
13	Williamson, A.	....	...	145	Rapid	Fuming sulph. acid	PCl_5	C
15	Schiff	....	...	140–150	...	Fuming sulph. acid	PCl_5	C
17	Baumstark	....	4.10	145–156 (mainly 150–152)	Rapid	Fuming sulph. acid	PCl_5	C
18	Williams	....	4.56	....	...	Fuming sulph. acid	PCl_5	C
19	Schützenberger	....	...	130	Rapid	Solid	CCl_4	P
20	Armstrong	....	...	141–145	Slow	Solid	CCl_4	P
21	Prudhomme	....	...	140	...	Solid	C_2Cl_6	P
22 (1)	Michaelis	1.819 (18°)	...	143	Slow	Solid	PCl_5	P
22 (2)	Michaelis	1.776 (18°)	...	158.4	...	Fuming sulph. acid	PCl_5	C
29	Clausnizer	....	...	150–151	...	Fuming sulph. acid	PCl_3+Cl_2	C
30 (1)	Thorpe	1.8585 (0°/4°)	...	139.6	...	Solid	S_2Cl_2	P
30 (2)	Thorpe	1.7847 (0°/4°)	...	155.3	...	Fuming sulph. acid	$POCl_3$	C

31	Ogier	....	3.70 (184°)	140.5	Slow	Vapor (?)	S_2Cl_2	P
33 (1)	Konovaloff	1.872 (0°)	7.31 (184°)	153	Slow	Solid	CCl_4	P
33 (2)	Konovaloff	....	4.10 (210°)	140–146	...	....	See below	Equal parts
33 (3)	Konovaloff	....	4.07	139–140	...	....	See below	C
35	Heumann and Köchlin	....	5.84(184°) 2.57(400°)	145–147	...	Vapor (?)	S_2Cl_2	P
37	Konovaloff	....	7.2 (210°)	152–153	...	Solid	S_2Cl_2	P
39	Moureau	....	...	130–157	...	Sulphuric acid	$SOCl_2$	C
41	Beckurts and Otto	....	...	151.7–152.7 (mainly)	...	Fuming sulph. acid 39% SO_3	HCl	C No P
47 (1)	Billitz and Heumann	....	5.89	145–147	Slow	....	See below	P
47 (2)	Billitz and Heumann	....	...	154–158	Rapid	....	See below	C
48 (1)	Besson	....	...	53 (15 mm.) 142–143	...	Not stated	Not stated	P
48 (2)	Besson	....	...	65 (15 mm.) 152	...	Not stated	Not stated	C
49	Prandtl and Borinski	1.876 (0°) 1.844 (18°)	7.21	150	Slow	Solid	See below	P

P = pyrosulphuryl chloride; C = chlorsulphonic acid.
In only one case, No. 41, was the actual amount of water in the sulphur trioxide or fuming sulphuric acid stated.
In No. 9 the crude product was distilled with sodic chloride, but the amount of the latter was not stated.
In No. 47 (1) chlorsulphonic acid was treated with phosphorus pentoxide.
In No. 47 (2) and No. 33 (3) pyrosulphuryl chloride was treated with water; in No. 49 with ice.
In No. 33 (2) equal parts of the two bodies were mixed.
The only properties mentioned of the product prepared with hydrochloric acid are those given in No. 41.

ing properties obtained by this long list of observers renders a revision of the constants desirable.

In deciding upon the purity of the products too much reliance has been placed by most investigators on the analysis. The difference between the two molecular weights, 233 and 215, is so small that even a very careful analysis might not detect a sufficient admixture of one body to influence the properties of the other (*v.* Table III, p. 713), nor show contamination by a slight amount of the products into which each body is easily decomposed.

In the separation and purification we have found most suggestive the early statements of Rose concerning the action of fused sodic chloride, the distillation under diminished pressure and the determination of the solidifying points as suggested by Besson. As a test of purity we have paid little attention to the analysis, but have relied upon the wide difference in melting points, the specific gravity, the action with water, the characteristic appearance of the two bodies in the solid state, and the color reactions with tellurium and selenium as given by Prandtl and Borinski.

General Methods for the Preparation of Pyrosulphuryl Chloride and Chlorsulphonic Acid.

The reaction of Schützenberger,[19] in which sulphur trioxide is acted upon by excess of carbon tetrachloride, is the one best adapted to the preparation of pyrosulphuryl chloride, since the reaction runs more nearly to completion, and excess of reagent is easily removed. While the presence of chlorsulphonic acid has been suspected or shown by other investigators in the crude product, yet it has not been definitely pointed out that the hydration of the sulphur trioxide would determine the proportion of each body in the mixture, at least roughly, and that by varying the strength of the sulphur trioxide a preponderance of either body may be secured. This we have found to be true, and we can therefore say, in general, that either pyrosulphuryl chloride or chlorsulphonic acid may be made by the Schützenberger method. The proportions of each body theoretically formed in the reaction by using different concentrations of sulphur trioxide are given in the following table, though it will be shown that these proportions do not hold good when the concentration of the sulphur trioxide is less than 89 per cent.

TABLE II.

THEORETICAL PROPORTIONS OF PYROSULPHURYL CHLORIDE AND CHLORSULPHONIC ACID FROM DIFFERENT CONCENTRATIONS OF SULPHUR TRIOXIDE.

Concentration.			Schützenberger Reaction (*a. c.*).				Per cent H_2SO_4.	Per cent excess.	Williamson Reaction (*b.*). 100 parts $zSO_3 \cdot yH_2O$ give Chlorsulphonic Acid.
Formula.	Per cent H_2O.	Per cent SO_3.	100 parts $zSO_3 \cdot yH_2O$ give		Per cent in Product.				
			Pyrosulphuryl Chloride.	Chlorsulphonic Acid.	Pyrosulphuryl Chloride.	Chlorsulphonic Acid.			
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
1. $2SO_3.3H_2O$	25.23	74.77	...	...	...	...	91.59	8.41 (H_2O)	...
2. $SO_3.H_2O$	18.37	81.63	...	59.4	...	100.0	100.00	...	...
3. $3SO_3.2H_2O$	13.04	86.96	...	105.5	...	100.0	70.99	29.01 (SO_3)	42.2
4. $2SO_3.H_2O$	10.11	89.89	...	130.8	...	100.0	55.04	44.96	65.4
5. $3SO_3.H_2O$	6.98	93.02	41.6	90.3	31.5	68.5	38.00	62.00	90.3
6. $4SO_3.H_2O$	5.33	94.67	63.5	69.0	47.9	52.1	28.95	71.05	103.4
7. $5SO_3.H_2O$	4.30	95.70	77.2	55.6	58.1	41.9	23.41	76.59	111.5
8. $10SO_3.H_2O$	2.20	97.80	105.1	28.5	78.7	21.3	11.97	88.03	128.1
9. $20SO_3.H_2O$	1.10	98.90	119.7	14.2	89.4	10.6	5.99	94.01	136.8
10. $50SO_3.H_2O$	0.45	99.55	128.3	5.8	95.7	4.3	2.45	97.55	142.0
11. SO_3	0.00	100.00	134.3	...	100.0	0.0	0.00	100.00	145.5

a. Limit for formation of chlorsulphonic acid by the Schützenberger reaction:

$$2SO_3 + 3H_2O + CCl_4 = 2H_2SO_4 + COCl_2 + 2HCl$$

b. Limit for formation of chlorsulphonic acid by the Williamson reaction:

$$SO_3 + H_2O + HCl = H_2SO_4 + HCl$$

c. Limit for formation of pyrosulphuryl chloride by the Schützenberger reaction:

$$2SO_3 + H_2O + CCl_4 = 2SO_2HCl + COCl_2$$

From the reaction

$$(1)\ 2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$$

we should have only pyrosulphuryl chloride when the sulphur trioxide is absolutely anhydrous, as Konovaloff [33] and others have shown. But from the reaction

$$(2)\ 2SO_3 + H_2O + CCl_4 = COCl_2 + 2SO_3HCl,$$

(Reaction *c* of Table II.)

the moisture conditions of which are fulfilled by ordinary fuming sulphuric acid, $H_2S_2O_7$, we should theoretically get only chlorsulphonic acid as the product. We may assume in this case that pyrosulphuryl chloride would be at first formed according to (1) and then decomposed according to

$$(3)\ S_2O_5Cl_2 + H_2O = 2SO_3HCl.$$

If now we increase the hydration of the acid, we should expect the chlorsulphonic acid to be decomposed according to

$$(4)\ 2SO_3HCl + 2H_2O = 2H_2SO_4 + 2HCl.$$

The limit of this decomposition is shown by combining equations (1), (3), and (4):

$$(5)\ 2SO_3 + 3H_2O + CCl_4 = COCl_2 + 2H_2SO_4 + 2HCl$$

(Reaction *a* of Table II.)

and we should expect no chlorsulphonic acid to be formed at a concentration equivalent to $2SO_3{\cdot}3H_2O$.

With a weaker acid, however, the greater concentration of the water causes a greater proportional decomposition of the chlorsulphonic acid and a larger amount of sulphuric acid; in other words, less sulphur trioxide is effective in attacking the carbon tetrachloride. Hence, as the proportion of water in the acid increases, there is less than the theory of chlorsulphonic acid found, more sulphuric acid left, and the limit of the formation of chlorsulphonic acid is reached sooner. The maximum effect (Preparation 8, p. 696) appears to be at a concentration of between 22 and 23 per cent of water. From 100 parts of the monohydrate, SO_3H_2O (18.37 per cent water) we should get about 22 parts of chlorsulphonic acid instead of 59.4 parts (Preparation 9) as would appear from Table II. From 100 parts of the hydration $3SO_3{\cdot}2H_2O$ (13.04 per cent water), there would be about 52 parts of chlorsulphonic acid instead of 105.5 parts (Preparation 7).

Now, as the concentration of the acid decreases to the hydration $2SO_3 \cdot H_2O$ (10.11 per cent water) there is less and less tendency to de-

composition of the chlorsulphonic acid, and the latter approaches closely to its theoretical maximum at this point, as shown by Preparation 2, p. 695. This is indicated also in Preparations 1 and 2 by the small amount of sulphuric acid left in the reaction.

In view of the fact that chlorsulphonic acid has a greater avidity for water than pyrosulphuryl chloride (p. 714), reaction (3) may not be entirely completed before its product is acted upon according to reaction (4). Hence the limit of the formation of pyrosulphuryl chloride may not be exactly at the hydration $2SO_3 \cdot H_2O$ (reaction *c* of Table II), but at a somewhat greater concentration of water. This is indicated by the yield of pyrosulphuryl chloride in Preparations 1 and 2, which is higher than would be expected. Conversely, the yield of chlorsulphonic acid would be less at this concentration. The amount of sulphuric acid would be greater, which is borne out also by these preparations.

The hydration of the sulphur trioxide will similarly influence the chlorination by sulphur monochloride according to the reactions: —

$$(1)\ 5SO_3 + S_2Cl_2 = 5SO_2 + S_2O_5Cl_2$$
$$(2)\ 5SO_3 + S_2Cl_2 + H_2O = 5SO_2 + 2SO_3HCl.$$

Here, while the reaction is complete, the boiling point of the sulphur monochloride is so near to that of each of the two bodies as to make purification by distillation practically impossible. With the chlorides of phosphorus, the reactions not only do not run to completion, but the purification of the product is complicated by the presence of phosphorus bodies. The use, therefore, of the chlorides of sulphur and phosphorus is of no value, especially as carbon tetrachloride is now so cheaply obtained.

We have found that the separation of the pyrosulphuryl chloride and chlorsulphonic acid formed in the Schützenberger reaction is completely accomplished by the addition of fused sodic chloride in excess and subsequent distillation under diminished pressure. The pyrosulphuryl chloride is unaffected by the sodic chloride and is distilled off. The chlorsulphonic acid is converted to its sodium salt, remains in the distillation residue, and may even be regenerated from this by distillation with fuming sulphuric acid. The recovery is not advantageous, however, owing to the difficulty of purifying the product. We have also found that pyrosulphuryl chloride may be separated in a mixture of the two bodies by crystallization. When the mixture is cooled and centrifugally filtered below the melting point of pyrosulphuryl chloride (*ca.*—37°), a very pure product is obtained, — the chlorsulphonic acid, with some pyrosulphuryl chloride, remaining entirely in the filtrate.

This method, however, is not practicable for any but small amounts, and there is danger of contamination by the moisture of the air.

In the preparation of chlorsulphonic acid the best method is the treatment of sulphur trioxide with hydrochloric acid, which must be ascribed to A. Williamson,[13] though first put in practical form by Beckurts and Otto.[41] Most convenient is a liquid oleum containing as much sulphur trioxide as possible according to the reaction :

$$H_2SO_4 + SO_3 + HCl = H_2SO_4 + SO_3HCl.$$

No pyrosulphuryl chloride can be formed, and the product is made practically pure by distillation with hydrochloric acid.

While chlorsulphonic acid may be formed under certain conditions by the addition of water to pyrosulphuryl chloride, the reaction does not serve as a method of preparation. Similarly, though dehydration of chlorsulphonic acid by phosphorus pentoxide takes place, it is only partial and hence of no advantage as a means of preparing pyrosulphuryl chloride.

The Preparation of Pyrosulphuryl Chloride.

The procedure adopted by us in treating sulphur trioxide with carbon tetrachloride according to the method of Schützenberger is as follows : — A round-bottomed flask of suitable size is sealed to the tube of an upright condenser, the upper end of the tube being carried some distance above the jacket of the condenser. A few centimeters below the top of the tube is sealed a side-tube of smaller bore, leading to a flue. An absorption bottle for the phosgene may be used here if desired. Through a rubber stopper in the top of the condenser tube and leading below the side-tube passes a separating funnel.

The oleum is prepared from an ordinary fuming acid by the addition of the requisite amount of solid sulphur trioxide, the proportion of the last in the mixture being determined by titration. For analysis, the oleum is weighed in a thin glass bulb, sealed after being filled. The bulb is broken under considerable water in a tightly stoppered bottle, the contents of which, when homogeneous, are made up to a definite volume. The carbon tetrachloride is a crude commercial product, dried over calcic chloride.

The dry apparatus is placed on a steam bath and carbon tetrachloride added through the condenser tube. The separating funnel containing the oleum is placed in position. The flask is then heated gradually and the oleum is run in slowly, the rate of addition being governed by the evolution of phosgene. After the addition of the

oleum, the heating is continued for some time after the evolution stops. The proportion of carbon tetrachloride to oleum should be about two to one.

As a partly solid oleum or "anhydrous" sulphur trioxide is less easy to handle, we have preferred to use as strong a mixture as will remain liquid at ordinary temperature,[50] though the yield of pyrosulphuryl chloride is less. If one wishes to use the stronger reagent, however, the apparatus may be so modified that the top of the condenser tube is sealed and the separating funnel containing the melted trioxide is connected directly with the flask by means of a two-holed rubber stopper, through the second hole of which passes the condenser tube instead of being sealed to the flask. Without this arrangement the melted substance would solidify in passing through the condenser.[51]

The contents of the flask are transferred to a distilling flask and fractioned; the first portion, up to 120° or 130° containing a little phosgene and excess of carbon tetrachloride, being rejected. The second fraction, which may run to 160°, is best redistilled and that portion boiling above 130° submitted to the following separation: — The mixture is placed in a roomy distilling flask, cooled by ice, and treated with small portions of fused, powdered sodic chloride, dried before use by heating to *ca.* 150° and cooled in a closed bottle. The amount necessary is calculated from the amount of water in the oleum and hence the probable quantity of chlorsulphonic acid present. From ten to twenty per cent in excess of that called for by the following equation is necessary.

$$SO_3HCl + NaCl = SO_3NaCl\,^{52} + HCl.$$

When the evolution of hydrochloric acid has ceased, and this may be promoted at the end by gentle warming, the pasty or partly dry mass is distilled under about 20 or 30 mm. pressure. For this purpose we extend the side-tube of the flask by sealing on a tube of about 50 cm., which is then surrounded by a short condenser jacket. Over the end of the lengthened side-tube is slipped a distilling flask of suitable size, fastened by a rubber stopper so that the end of the tube dips into the belly of the flask. The side-tube of the receiver is connected with the exhaust and manometer; a system of absorption tubes filled with stick

[50] From 92.5 to 95 per cent total SO_3.

[51] See also Preparation 6, p. 696.

[52] For the preparation and analysis of sodic chlorsulphonate, see Ruff (note 45, p. 681).

sodic hydroxide being interposed as a precaution against corrosion by the acid vapors. The flask containing the reaction mixture is closed by a rubber stopper carrying a thermometer, and is about three-quarters immersed in an oil bath, the temperature of which is controlled by a second thermometer. The suction is applied until the hydrochloric acid is drawn off, and the oil bath is then gradually heated. The pyrosulphuryl chloride in the mixture distils with little or no decomposition, leaving the sodic chlorsulphonate as a dry mass. The oil bath, as distillation slackens, is kept for some time at a somewhat higher temperature than the boiling point of the pyrosulphuryl chloride, but a considerable amount of the latter adheres to the residue.

The product thus obtained melts after solidification within a few degrees of the proper point, and a single rectification over a small quantity of fused sodic chloride under diminished pressure is usually sufficient to give a perfectly pure product.

Regeneration of the Chlorsulphonic Acid. — We at first thought that it would be practicable to recover from the sodium salt residue the chlorsulphonic acid of the original reaction product, — even perhaps to use the Schützenberger method for the preparation of both bodies by employing an oleum of suitable strength. While by distillation of the residue with excess of fuming sulphuric acid according to the equation

$$SO_3NaCl + H_2S_2O_7 = SO_3HCl + NaHS_2O_7$$ [53]

the chlorsulphonic acid is indeed regenerated, it is in an impure state and its purification is not worth while, since a pure product is so easily obtained by the Williamson method.

The Properties of Pyrosulphuryl Chloride.

Pyrosulphuryl chloride is a colorless liquid, fuming slightly in moist air and becoming turbid when added to a small amount of water. It sinks in water as an oil, gradually decomposing into chlorsulphonic acid, which in turn gives sulphuric and hydrochloric acids as final products. Chlorine and probably sulphur dioxide may be formed in small amount. It boils at 152.5° to 153° at 766 mm., and is not appreciably dissociated at this temperature, if perfectly dry, but complete absence of moisture is difficult to secure, as the substance is very hygroscopic. At a pres-

[53] We do not assume the formation of such a salt, though it is supposed to exist (e. g., Schultz-Sellac, Ber., **4**, 109 (1871)). The reaction is, however, more complete when the fuming sulphuric acid is in this proportion.

sure of 19 mm., it boils at 56–57° without decomposition. It crystallizes easily at low temperature and melts at −37.5° to −37°. The specific gravity at 20°, referred to water at 4°, is 1.837; at 0° (water at 4°), 1.872. There is no appreciable dissociation at the boiling point of aniline. It is not colored by the addition of finely divided tellurium or selenium.

For the properties of mixtures of pyrosulphuryl chloride and chlorsulphonic acid, see page 712 and Table III (page 713).

The Preparation of Chlorsulphonic Acid.

In carrying out the Williamson reaction

$$H_2SO_4 + SO_3 + HCl = H_2SO_4 + SO_3HCl,$$

the oleum should contain as much sulphur trioxide as possible. It is placed in a roomy distilling flask, closed by a three-holed rubber stopper and mounted on a tripod. Through one hole of the stopper passes a right-angle tube slightly constricted at its lower end, extending to the bottom of the flask. Through the second hole is attached a distilling tube in one piece, surrounded by a condenser jacket, and the third hole carries a thermometer.

The hydrochloric acid gas is conveniently generated by slowly adding crude, concentrated sulphuric acid from a dropping funnel to crude concentrated hydrochloric acid contained in a generating flask. The gas is carefully dried by passing at least two Emmerling towers containing glass beads saturated with concentrated sulphuric acid, and a U-tube with phosphorus pentoxide. The gas is passed through the oleum slowly, at room temperature, until there is no further evidence of absorption, the flask and condenser being inclined so that any condensed vapor may run back. At the end, the contents of the flask are distilled in a current of dry hydrochloric acid gas, the portions distilling below 145° and above 160° being rejected. A rectification of the middle portion in hydrochloric acid results in a product of sufficient purity for all purposes for which the substance may ordinarily be required, but an absolutely pure product is obtained only by crystallization at low temperature, as will be shown in the Experimental Part.

The Properties of Chlorsulphonic Acid.

Chlorsulphonic acid is a colorless liquid which fumes very strongly in moist air. If added to water, it reacts with explosive violence, and is immediately decomposed into hydrochloric and sulphuric acids. Chlorine and sulphur dioxide are also formed in small amount. It cannot

be boiled without partial dissociation, but, when equilibrium sets in, the boiling point is about 151–152° at 765 mm. The slight dissociation is partly into hydrochloric acid and sulphur trioxide (which react partially to form water, sulphur dioxide, and chlorine); partly to sulphuryl chloride and sulphuric acid. The latter dissociation may be brought about at the boiling point by a catalyser. At a pressure of 19 mm. it boils at 74–75°, but the dissociation into hydrochloric acid and sulphur trioxide is increased; still more at from 2 to 4 mm., the boiling point being then approximately 60–64°. At the boiling point of aniline, the dissociation, though not complete, amounts to about two volumes. It crystallizes readily at low temperature and melts at −81° to −80°. The crude acid requires a lower temperature for solidification, changing into a vitreous body, which becomes viscous at about −130° to 125° and sometimes partly crystalline. The specific gravity at 20°, referred to water at 4°, is 1.753; at 0° (water at 4°), 1.784. With finely divided tellurium, chlorsulphonic acid gives a cherry-red color, which persists for several hours, fading gradually to purple, then pink, and becoming finally colorless. With finely divided selenium, it gives a moss green color, which gradually becomes a fainter green, then yellow, and finally colorless.

For the properties of mixtures of chlorsulphonic acid and pyrosulphuryl chloride, see page 712 and Table III (page 713).

Experimental.

Preparations of Pyrosulphuryl Chloride.

1. 105 g. oleum (90 per cent SO_3) were added to 110 g. CCl_4 (10 per cent over theory) in an hour. 22 g. distillate were obtained up to 130°; 83 g. from 130° to 155° (chiefly 150–152°), and the residue was less than 2 g. The main fraction melted at −128° and was chiefly chlorsulphonic acid. This was treated with 50 g. fused sodic chloride and distilled, a U-tube [54] in liquid air being placed after the receiver. 9 g. distillate were obtained from 53° to 60° (26 mm.); the U-tube contained a little hydrochloric acid. The melting point of the distillate, −39°, showed a fairly pure pyrosulphuryl chloride. The dry residue was treated with 125 g. oleum (91 per cent SO_3) and distilled, a bottle cooled by ice and salt being placed before the U-tube in liquid air. At 78–87° (23 mm.) 46 g. of distillate were obtained, melting at −128–125°, s. g. 1.767 at 20°. In the cooled bottle was a little sulphur trioxide, in the U-tube a little hydrochloric acid.

The yield of chlorsulphonic acid is low owing to insufficient carbon

[54] Figure 1, p. 697.

tetrachloride, for much of this reagent escapes with the phosgene. The pyrosulphuryl chloride is high, but it is clear that both bodies are formed in the reaction and that chlorsulphonic acid is the chief product.

2. 116 g. oleum (90 per cent) were added to 225 g. CCl_4 (over twice the theory) in 45 minutes, and the mixture fractioned after standing over night. From 65° to 130°, 112 g. were obtained; from 145° to 153°, 137 g., melting at —128°. There was little residue. The 137 g., treated with 81 g. salt (120 per cent theory) gave 14 g. distillate at 56–57° (23 mm.) melting at —37–36°. The residue was not examined. The yield of crude mixture, 91 per cent, has been improved by excess of carbon tetrachloride, and it is again shown that only a small amount of pyrosulphuryl chloride is formed from a low oleum.

3. 108 g. melted SO_3 (98.9 per cent) were added to 220 g. CCl_4 in 45 minutes and fractioned after 48 hours. 165 g. were obtained up to 130°; 106 g. from 139° to 141°, and there was little residue. By redistilling the first fraction, a little more was added to the second, giving 110 g., boiling mainly at 140°, melting at —41–40°. This treated with salt and distilled gave 84 g. at 60° to 62° (25 mm.), melting at —38–35°. The residue was not examined. The yield of crude pyrosulphuryl chloride, 84 g., is about 70 per cent of the theory.

4. 175 g. oleum (93.4 per cent) were added to 347 g. CCl_4 in 90 minutes, the product standing over night. 176 g. were obtained up to 130°; 189 g. between 130° and 152°, and the residue was slight. The main fraction melted chiefly at —90°, but there was a residual solid not melting until —45–40°. 103 g. of the main fraction, with 50 g. salt (150 per cent theory) gave 39 g. distillate at 50–55° (21 mm.), melting at —43–38°. The distillation was continued up to 80° (bath, 150°), which evidently caused decomposition, as there was much hydrochloric acid in the U-tube, a little chlorine, and, from its melting point, considerable sulphuryl chloride. The residue from the salt treatment was distilled with 130 g. oleum (89.3 per cent), slightly in excess of the theory. At 70–76° (21 mm.), most of the product, 64 g., came over, but the heating was continued to 87° (bath, 153°). The U-tube contained hydrochloric acid, chlorine, and sulphuryl chloride. On redistillation, 56 g. were obtained at 75–78° (23 mm.), melting at —133–127°. Considerable sulphuric acid was left in the flask, and in the U-tube was some sulphuryl chloride. The yield of crude mixture, 189 g., is about 75 per cent of the theory. The proportions of the two bodies, 39 g. and 56 g., are in the direction of those which should have been recovered from 103 g. of crude mixture, —36 g. and 67 g. The decomposition of the chlorsulphonic acid was in accord with the observations of other workers and with those made later by ourselves.

5. 445 g. oleum (93.2 per cent) were added to 496 g. CCl_4 (138 per cent) in two hours, and the product stood over night. 131 g. were obtained up to 135°; 497 g. from 135° to 150°, little being left in the flask. A second fractionation increased the fraction from 135° to151° to 534 g., melting at —120–115°, but redistillation gave 474 g. from 134° to 154°. This is 81 per cent of the theory. 134 g. of the product, with 65 g. salt (50 per cent excess) gave 31 g. boiling at 40–49° (19–23 mm.) and melting at —37°. The sodium salt, with fuming acid, gave 65 g. crude chlorsulphonic acid boiling at 80–85° (25 mm.). According to Table III we should expect 45 g. and 89 g. respectively.

6. 300 g. melted SO_3 (98.9 per cent) were covered with 572 g. CCl_4 in a one-liter flask provided with a long condenser and placed on a sand bath. There was but slight action in the cold; on gentle heating for two hours the reaction was complete. After distilling off the excess of CCl_4, very little came over up to 135°; nearly all distilled from 135° to 141°. Yield 345 g. or 85 per cent. On treatment with 50 g. salt, there was little evolution of hydrochloric acid, and, on distillation at atmospheric pressure, most of the product came over at 149°. Redistillation at 76° (74 mm.) with a second quantity of salt gave a very pure product, melting at —37° (corr.). This is Sample C, page 699.

7. 150 g. sulphuric acid (85.9 per cent SO_3) were added to 300 g. CCl_4 and heated for 10 hours. The product was homogeneous. On distillation, 40 g. were obtained up to 120° and 74 g. from 120° to 158°, which, from its appearance and action with selenium and tellurium, was chiefly chlorsulphonic acid. The residue, 100 g., was sulphuric acid.

8. 150 g. sulphuric acid (77.0 per cent SO_3) were added to 300 g. CCl_4 and heated for 10 hours. There was no evidence of phosgene during the heating and the product separated into two layers. 279 g. CCl_4 were recovered, with faint odor of phosgene. The fraction from 90° to 140° weighed 5 g.; that from 140° to 160°, 3 g., and neither gave any test for chlorsulphonic acid. The residue, sulphuric acid, weighed 141 g.

9. 100 g. sulphuric acid (82.0 per cent SO_3) were heated with 200 g. CCl_4 for 5 hours. Phosgene was given off and the product was homogeneous. After distilling off excess of CCl_4, a fraction of 2.5 g. was obtained from 150° to 153°; a second, of 22.5 g., from 153° to 160°. Both were evidently chlorsulphonic acid, from appearance and tests. The residue, sulphuric acid, weighed 80 g.

It is clear that the two bodies are formed practically in proportion to the hydration of the oleum used, provided the concentration of the sulphur trioxide is at least 89 per cent. Below this percentage no

pyrosulphuryl chloride results, and the yield of chlorsulphonic acid is rapidly diminished by the increasing proportion of water. The economic preparation of pyrosulphuryl chloride demands an oleum containing at least 95 per cent of sulphur trioxide and a large excess of carbon tetrachloride.

The purification of the products of some of these preparations is given in the following.

Purification of Pyrosulphuryl Chloride and Determination of Constants.

Boiling Point. — 106 g. of crude substance from Preparation 5 were twice distilled over salt, and 70 g. were obtained boiling at 55–57° (18 mm.), with melting point of —38–35° (corr.). This product was then distilled into a 3-way Bredt[55] receiver, the arms of which carried (1) a small distilling flask, (2) a Y-tube in which samples could be sealed off for analysis, melting point, and vapor density, and (3) a flask adapted to the arm of the pyknometer in which the specific gravity was to be determined. The entire distillate came over at 56–57° (19 mm.) Sample A.

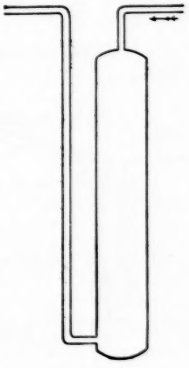

FIGURE 1.

15 g. of the above were distilled from an oil bath in the flask in which they were collected. The thread of the corrected thermometer was entirely in the vapor. A U-tube[56] in liquid air was connected with the receiver. Distillation began at 142°, the thermometer rose rapidly, and all came over mainly at 152–153° (766.6 mm., corr.). The U-tube contained some barely visible white specks, melting at room temperature with odor of sulphur dioxide. 50 g. of the original distillate, some of which had been open to the air, were also distilled. While the boiling point was again chiefly from 152° to 153°, it was not perfectly constant, and there was more

[55] Anschütz, d. Destillation unter vermindertem Druck, 1895.

[56] These U-tubes, the construction of which is clear from Figure 1, are readily made from pieces of wide and narrow tubing to fit the Dewar liquid air container. The position of the side-tube prevents its being clogged by solids. By rapid work weighings can be made within half a gram; condensed gases are evaporated at room temperature, liquids may be poured off, and a residual solid weighed in its turn. Very satisfactory approximations may be made in this way.

evidence of decomposition in the form of unweighable white and yellow specks from which a test for chlorine was obtained.

The 84 g. from Preparation 3 were then distilled with 20 g. salt at low pressure, with special precautions against access of moisture, as provided by the apparatus shown in Figure 2. Dry air was passed through the system for 2½ hours and the glass was gently warmed. The inlet tube at A was then sealed off, the system exhausted, and the liquid distilled from F to F'. After about 60 g. had come over at 63–68° (25 mm.), with some evidence of decomposition products in the U-tube, the heating was discontinued and the tube sealed off at B. The 60 g. were then distilled at 766 mm., corr., a well-dried flask and another U-tube in liquid air being added at C. The first few drops came over at 148–150°, and all the remainder from 152.5° to 153°. There were only faint specks in the U-tube. Sample B.

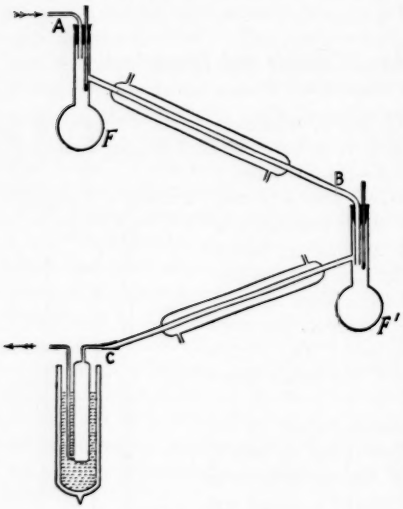

FIGURE 2.

From these two results the boiling point of pyrosulphuryl chloride may be placed at 152.5° to 153° at 766 mm. There is probably a tendency to slight decomposition at the boiling point, since the absolute exclusion of moisture from such a substance is well nigh impossible.

Specific Gravity. — The specific gravity of Sample A was taken by means of a carefully calibrated Ostwald pyknometer from a portion sealed until use.

1. At 20°, 14.0408 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8352

2. At 20°, 14.0401 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8351

From Sample B, the following figures were obtained:

3. At 20°, 14.0425 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8354

4. At 20°, 14.0508 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8365

The specific gravity of Sample C (Preparation 6) after taking a melting point determination, was 1.8364 at 20°, referred to water at 4°. It was again distilled with salt under diminished pressure. Of this product,

5. At 20°, 14.0538 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8369

6. At 20°, 14.0525 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8367

7. At 0°, 14.3292 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0°}{4°}$ 1.8718

8. At 0°, 14.3277 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0°}{4°}$ 1.8716

(The data above are corrected in order to give the figures for specific gravity: weights of water to 4°, all weights to vacuum.)

The specific gravity of pyrosulphuryl chloride at 20°, referred to 4°, is therefore 1.837; at 0°, referred to water at 4°, 1.872.

Melting Point. — The determination of this constant, which plays a very important part in the purification of pyrosulphuryl chloride and chlorsulphonic acid and their differentiation, was made in two ways. The first method, particularly available for small quantities of substance, is analogous to that so commonly employed in the determination of the melting point of organic substances, in which the material is placed in a thin-walled "capillary" tube, closed at one end. This we shall refer to as the "capillary method." In the second, which we shall call the "immersion method," the thermometer is placed in a test tube containing a comparatively large quantity of substance, so that the entire thread may be covered by the substance when melted.

A Rothe[57] thermometer filled with pentane was used, 35 cm. long, graduated from 30° to −200° in whole degrees. As this was grad-

[57] Zeitschr. f. Instrumentenkunde, **24**, 5 (1904).

uated for complete immersion and in the capillary method most of the stem would be outside the bath, the reading was several degrees too high. For this method, therefore, the standardization of the instrument was based upon a definite depth of bulb immersion, the substance being always level with the bulb. As fixed points there were taken, at several room temperatures, the boiling point of oxygen (−182.8°), the sublimation point of a thin, homogeneous mixture of carbon dioxide and absolute alcohol (−78.3°), and the melting point of pure mercury (−39°).[58] The corrections thus determined were well suited for temperatures between −100° and −50°, but in the region of −28°, the uncorrected melting point of pyrosulphuryl chloride, the variation for a degree in the stem temperature (determined by a mercury thermometer alongside) was considerable. To avoid troublesome corrections at this point, the melting point of pure mercury was taken in the same manner and at the same time as that of the sample. As the melting points of mercury and pyrosulphuryl chloride differ by only two degrees, the correction could fairly be assumed to be the same for each. In the immersion method, the fixed points were the boiling point of oxygen, the sublimation point of the carbon dioxide-alcohol mixture, and the temperature of melting ice; corrections being made from a curve plotted from these.

The bath used was a naphtha, liquid and mobile at −150°, contained in a small beaker, which in turn was immersed in a beaker of liquid air. The inner beaker was covered by a stout filter paper, fastened under the rim in order to prevent the naphtha from becoming opaque through condensation of moisture and carbon dioxide. The filter paper was provided with suitable holes for the thermometer, concentric stirrer, etc.

The liquid to be tested is introduced into the capillary tube by warming and cooling the latter; sometimes the powdered frozen liquid can be added in the ordinary way. In either of the two methods, capillary or immersion, the tubes are placed in the bath and the liquid in them solidified under stirring of the bath. The liquid air beaker is then lowered and the temperature of the bath allowed to rise as slowly as possible, under careful stirring. This retardation, which may be accomplished by the approximation of the liquid air, is necessary, as otherwise the bath may rise several degrees in one minute and a fusion may take place between too great extremes. The rising thread is always read, and care is taken to see that it is unbroken, a frequent danger in these instruments.

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[58] Constants from Ostwald-Luther, Hand- und Hülfsbuch, 1910.

Two portions of Sample A, the second having remained sealed until used, gave respectively −38° to −37° and −37.5° to −37°, by the capillary method. Of Sample B a portion melted from −37° to −34.5° by the immersion method. Further precautions in using this method were taken in the examination of Sample C. The tube containing the substance was provided with a two-holed rubber stopper, through one hole of which passed the thermometer. The other hole carried a T-tube, through the vertical portion of which moved the stirrer. Into the side arm was passed a gentle current of dry air, to prevent access of moisture to the substance. The melting tube was immersed in a bath of alcohol at a temperature two to four degrees higher than that of the substance. Four determinations with Sample C gave an average of −37.3°.

The melting point of pyrosulphuryl chloride may be placed, therefore, at −37.5° to −37°.

Vapor Density. — The determinations of vapor density were made by the Victor Meyer method at the temperature of boiling aniline (184°). The weighing bulbs and the apparatus were very carefully dried and the eudiometer calibrated. Readings of the volume of air replaced were not made until the meniscus had long remained constant. The following results were obtained:

Substance.	C.c. Air Replaced.	T°.	Bar. Corr.	Vapor Density.
1. Sample A 0.0480 g.	5.72	21	739.8	7.2
2. Sample A 0.2102 g.	27.53	23	742.6	6.6
3. Sample A 0.0625 g.	6.90	23.3	736.8	7.8
4. Sample C 0.1382 g.	16.95	26.5	744.6	7.1
5. Sample C 0.2501 g.	28.90	27.5	742.6	7.5
Calculated for $S_2O_5Cl_2$				7.49

These determinations show that pyrosulphuryl chloride does not dissociate appreciably at a temperature of 184°, and it is less likely to do so at its boiling point. The presence of traces of moisture, which are not easy to guard against, would lower the vapor density slightly. In this connection, the addition of phosphorus pentoxide to the bulb of the Meyer apparatus by Prandtl and Borinski [49] is not admissible in the presence of a possible impurity of chlorsulphonic acid, which would thereby be dehydrated.

Analysis. — A volumetric analysis was made of Sample B. 1.1657 g. substance were prepared for titration as in the analysis of oleum, p. 690.

1. 100 c.c. (1/5) of the solution required 35.88 c.c. KOH (0.9078 N/5)
2. " " " 35.88 c.c. KOH (0.9078 N/5)
3. " " " 21.74 c.c. $AgNO_3$ (N/1; Volhard)
4. " " " 21.69 c.c. $AgNO_3$ (N/1; Volhard)

A gravimetric analysis of Sample C resulted as follows:

5. 0.9400 g. substance gave 2.0352 g. $BaSO_4$
6. 1.0606 " " 2.3009 g. $BaSO_4$
7. 1.1917 " " 1.5891 g. AgCl
8. 1.1813 " " 1.5751 g. AgCl

	Found.	Calculated for $S_2O_5Cl_2$
Sulphur:	(1) 29.93, (2) 29.93, (5) 29.75, (6) 29.80	29.82
Chlorine:	(3) 33.14, (4) 33.07, (7) 32.99, (8) 32.99	32.98

Preparations of Chlorsulphonic Acid.

10. Dry hydrochloric acid gas was passed into 150 g. oleum (91.1 per cent) for two hours, the flask being kept cool by ice water. After expulsion of the hydrochloric acid, distillation between 149° and 170° (chiefly 152–155°) yielded 101 g. (theory, 113 g.), and the residue, which was practically all sulphuric acid, weighed 72 g. (theory, 73 g.). On treating the 101 g. with 60 g. salt and distillation under diminished pressure, only 1.5 g. were obtained, which, from melting point and action with water, appeared to be unchanged chlorsulphonic acid.

11. 165 g. oleum (89.3 per cent) were used. The flask was not cooled. The yield of distillate between 135° and 164° was 89 g. (theory, 100 g.), and the residue was 97 g. (theory, 96 g.).

12. 147 g. oleum (89.3 per cent) were treated as in Preparation 11. The product was then distilled in a current of hydrochloric acid, and 88 g. (theory, 89 g.) were obtained from 148° to 151°, the residue weighing 82 g. (theory, 86 g.).

13. 526 g. oleum (93.9 per cent) were saturated with hydrochloric acid as in Preparation 11. Of the total increase in volume, two thirds resulted from passing the gas rapidly for two hours, one third in an additional five hours. On distilling in hydrochloric acid, 528 g. were obtained, boiling chiefly from 150° to 154° (theory, 512 g.).

14. The oleum contained 86.2 per cent SO_3. The method was as in Preparation 11, but weights were not recorded.

15. 419 g. oleum (88 per cent) were used; the method was as in Preparation 11. 261 g. product were obtained, the distillation with hydrochloric acid being very slow (theory, 212 g.).

16. 333 g. oleum (85.3 per cent) were heated on the steam bath and

hydrochloric acid passed for seven hours. The product, distilled with hydrochloric acid, gave 107 g. distillate under 162° (theory, 97 g.).

17. 550 g. oleum (89.3 per cent), treated as in Preparation 16, gave on distillation with hydrochloric acid, 375 g., boiling mainly from 149° to 151° (theory, 333 g.).

The amount of chlorsulphonic acid formed in the Williamson reaction depends upon the percentage of sulphur trioxide in the oleum not combined as sulphuric acid. The sulphuric acid is unchanged. No pyrosulphuryl chloride is formed. Attempts to increase the yield from a low oleum by addition of phosphorus pentoxide during the chlorination, according to Müller,[28] were unsatisfactory. While the total weight of product was somewhat increased, yet it was probable that some pyrosulphuryl chloride was formed by the dehydration of the chlorsulphonic acid by phosphorus pentoxide.

The reaction mixture is best distilled in a current of hydrochloric acid. As will later be shown, the chlorsulphonic acid thus obtained is fairly pure and is made no purer by distillation, owing to the partial dissociation at the boiling point. A pure product is obtained only by crystallization, as will be shown.

Purification of Chlorsulphonic Acid and Determination of Constants.

The instability of chlorsulphonic acid under heating was to be inferred from the work of other observers, but we hoped to be able to purify it by distillation at reduced pressure, and proceeded for some time under that assumption. It became evident, however, that all our efforts to get a pure product by distillation, whether at normal or reduced pressure, were nullified by the invariable presence of decomposition products, and that the decomposition was relatively complex. While the subject requires further investigation, we may state here, however, the facts concerning the dissociation which appear most probable from our work and that of others.

The Dissociation of Chlorsulphonic Acid. — Under ordinary conditions of temperature and pressure, and in absence of moisture, chlorsulphonic acid is stable. If, however, it is subjected to diminished pressure or to increased temperature, or to a combination of the two, a partial breaking down occurs, which is proportional to the change of conditions. We regard this breaking down, from our own observations and those of others, as taking place primarily in two directions, which we may represent as follows:

(1) $2SO_2OHCl \rightleftarrows 2SO_3 + 2HCl$

and (2) $2SO_2OHCl = SO_2Cl_2 + SO_2(OH)_2$.

Following the analogy of the reduction of sulphuric acid by nascent hydriodic and hydrobromic acids, the products of reaction (1) are more or less changed according to

$$(3)\ 2SO_3 + 2HCl = SO_2 + Cl_2 + SO_2(OH)_2,$$

while the products of reaction (2) become, to a greater or less extent,

$$(4)\ SO_2Cl_2 + SO_2(OH)_2 = SO_2 + Cl_2 + SO_2(OH)_2;$$

hence the ultimate observed dissociation would be represented by

$$(5)\ 2SO_2OHCl = SO_2 + Cl_2 + SO_3 + H_2O,$$

the same result being reached in whichever direction the breakdown primarily started.

Under diminished pressure, at temperatures from 60° to 80°, we have found reaction (1) to take place, and in proportion to the decrease of pressure. The greater dissociation at the lower pressure is due, according to the principle of Le Chatelier, to the fact that the vapor increases in volume, and, indeed, the effect of a pressure as low as 1 to 4 mm. is to pump out the more volatile hydrochloric acid, hence that portion of the distillate which is condensed by liquid air (Figure 2) contains relatively much more hydrochloric acid than sulphur trioxide.[59] As we have found also sulphuryl chloride, sulphur dioxide, and chlorine among the products of distillation under diminished pressure, with a residue of sulphuric acid, we consider that reaction (2) occurs to a slight extent, and also reaction (3), though to a less degree than at higher temperatures.

At atmospheric pressure and at the boiling point, reaction (1) takes place, as Williams [18] and Ruff [45] have stated. But, while the primary action is less than at low pressure, the secondary action (3) is greater, and we find more sulphur dioxide and chlorine, with a larger residue of sulphuric acid, than under lower conditions of temperature and pressure. The presence of sulphuric acid, however, is partly accounted for by reaction (2), for we find sulphuryl chloride among the products of distillation at ordinary pressure, and, indeed, in greater quantity than when the pressure is low. That sulphuryl chloride is formed under these conditions was not recognized by Ruff, but he showed clearly that the presence of a catalyser brings about reaction (2) at the

[59] The presence of sulphur trioxide in chlorsulphonic acid distilled at this pressure was indicated by the analysis and specific gravity of the product, and was confirmed qualitatively and quantitatively on careful fractionation of the product at ordinary pressure.

boiling point, and, indeed, not only to the apparent exclusion of (1) and (3), but to the completion of (2).

In addition to the phenomena of dissociation as expressed by the above reactions, we have found that the sulphur trioxide formed by the dissociation dehydrates the chlorsulphonic acid to a slight extent, giving pyrosulphuryl chloride.[60]

$$(6)\ 2SO_2OHCl + SO_3 \leftrightarrows S_2O_5Cl_2 + SO_2(OH)_2.$$

As to the character of the dissociation at temperatures above the boiling point, we can ourselves offer no direct evidence. Behrend [44] obtained a good yield of sulphuryl chloride by heating in a closed tube at 170° to 180°, and considered that reaction (2) took place. Beckurts and Otto [41] explain the reaction by the equations

$$(7)\ 2SO_2OHCl = Cl_2 + H_2S_2O_6,$$
$$(8)\ H_2S_2O_6 = SO_2 + SO_2(OH)_2,$$
$$(9)\ Cl_2 + SO_2 = SO_2Cl_2.$$

Since they found chlorine and sulphur dioxide in the closed tube at 180°, reaction (9) would not be complete. But Ruff found the equilibrium at 170° in a closed tube to be

$$(2)\ \underset{2.5\ \text{mol.}}{2SO_2OHCl} \leftrightarrows \underset{1\ \text{mol.}}{SO_2Cl_2} + \underset{1\ \text{mol.}}{SO_2(OH)_2}$$

and lowered the temperature of complete decomposition to the boiling point by the catalyser. As in the presence of the catalyser Ruff found that no more sulphuryl chloride was formed by passing chlorine and sulphur dioxide into the boiling chlorsulphonic acid than without them, they were not essential to the formation of sulphuryl chloride, and reaction (9) evidently did not take place. It is also unnecessary to assume reactions (7) and (8) to explain the formation of sulphur dioxide and chlorine.

Ruff considered that at temperatures higher than 180° reactions (1) and (3) took place; Heumann and Köchlin [35] that chlorsulphonic acid was completely dissociated at 442°, according to reaction (5), but at 184° they found the dissociation incomplete.

That sulphuryl chloride, chlorine and sulphur dioxide are coëxistent products of the dissociation at temperatures short of that necessary for

[60] For the hydration of pyrosulphuryl chloride by sulphuric acid, *v.* p. 717.

complete dissociation is undoubted. Whether we shall ascribe the formation of the last two of these bodies to reactions (1) and (3) or to reactions (2) and (4) is immaterial. But it is not unreasonable to suppose that reaction (1), which at diminished pressure and comparatively low temperature is predominant over reaction (2), becomes not only secondary to reaction (2) at atmospheric pressure and higher temperature, but also that, at the highest temperatures noted, it would merge into reaction (5).

Whatever may be the mechanism of this rather complex dissociation, it is certain that distillation of chlorsulphonic acid at any pressure will result in a product which may contain, in varying amounts, sulphuryl chloride, chlorine, sulphur dioxide, sulphur trioxide, hydrochloric acid, and sulphuric acid. The disagreeing results of previous observers on the constants of chlorsulphonic acid are therefore easily explained, for their products, though often of sufficiently good quality for practical purposes, were contaminated by more or less of these dissociation products, and hence showed varying boiling points, specific gravities, etc.

By distillation with hydrochloric acid, reaction (1) obviously runs to the left, and there should be little tendency to dissociation. Ordinary distillation, at atmospheric or low pressure, will not purify. After realization of this fact, we turned to crystallization, as will be shown.

Behavior of Chlorsulphonic Acid under Distillation. — In Preparations 10 and 11 above, in which the distillation was without hydrochloric acid, the product is contaminated by the products of dissociation, and the apparent yield is less. In the others, there is a greater or less amount of hydrochloric acid present and probably less of the dissociation products.

The crude preparations of chlorsulphonic acid showed a very characteristic behavior on cooling. At −70° to −80°, the liquid becomes thicker and gradually viscous as the temperature falls. At −130° to −140° an amorphous, vitreous mass is formed, which under rising temperature becomes gradually viscous again from −140° to −120°, averaging, say, at −130°, and is limpid at about −85°. This behavior differentiates the substance sharply from pyrosulphuryl chloride, which gave definite crystals at −40° to −35°, and at −70° to −60° even when containing 90 per cent of chlorsulphonic acid. But, while the differentiation was clear, the melting evidently indicated impure chlorsulphonic acid.

Preparation 11 became viscous at −133–127°. At 24–27 mm. it boiled chiefly at 80–82°, and the solidified product softened at −125–117°. The specific gravity was 1.786 at 20°. To avoid the presence

of sulphuric acid, which was suggested by the specific gravity and boiling point of Preparation 11, the subsequent preparations were distilled with hydrochloric acid, as described above.

Preparation 12 boiled from 147° to 151°, became viscous at −138–130°, and had a specific gravity of 1.745 at 20°. Distilled at low pressure, it boiled from 77° to 81° (24–31 mm.), softened at −130–125°, with specific gravity of 1.765. Three more distillations at low pressure did not essentially change these properties, and the preparation was evidently as pure as this treatment was likely to make it. 29 grams boiled at 145–150.5° for the first half; 150.5–152° (762 mm.) for the second. The presence of white fumes of sulphur trioxide towards the end emphasized the decomposition, and about half a gram of residue was left, which was mainly sulphuric acid. A vapor density determination in aniline (184°) gave 2.6 and 2.4 (theory, 4.04). A volumetric analysis gave: chlorine, 30.00; sulphur, 28.02 (required, 30.43 and 27.52).

We did not study the decomposition in the course of these distillations by means of the liquid air tube (Figure 1) as in the subsequent trials. The product was probably more impure than would appear from the properties, for the impurities compensated each other to a certain extent. But the specific gravity and decomposition pointed to the presence of sulphur trioxide at least.

The study of the portion of Preparation 1 (46 g.), which had been recovered from its sodium salt, is now of interest. This was viscous at −128–125°, with specific gravity of 1.767 at 20°, and boiled at 78–87° (23 mm.). On distillation at atmospheric pressure, a few drops came over at 148–149°, but the greater part at 151–152°. There was some decomposition and a few drops of sulphuric acid were left. On distilling again, one fifth came over from 147° to 149°, the rest chiefly at 150–152°. A third distillation increased the amount from 146° to 150° to one half, the rest mainly from 150° to 153°. Little residue was left in the last two cases. The product now became viscous at −136–127°, but at −85° crystals appeared, which melted at −69°. The specific gravity was 1.755 at 20°. Two more distillations carried the beginning to 140°, a third to 100°, whence came a rapid rise to 144°, and two more distillations brought much under 100°. Sulphuric acid in small quantity was left in the flask each time, and there was evidence of chlorine. The melting point of the product was −126°; then crystals separated, melting at −70°. The specific gravity was 1.756. On distilling again, a few drops were collected below 100°. These gave an oil with water, dissolving quietly. The melting point was −51° (corr., −60°). This was evidently sulphuryl chloride and

not pyrosulphuryl chloride,[61] as shown by the boiling and melting points and by the low specific gravity.

Preparation 10, which was viscous at −124°, was regenerated from its sodium salt and studied with more care as to exclusion of moisture. It boiled at 73–75° (21 mm.), became viscous at −128–126°, and had a specific gravity of 1.767 at 20°. 60 grams of this were then distilled at atmospheric pressure until about one third came over. Of the remainder, about 10 grams were distilled at low pressure (t°, 63°, p., 24 mm.), a U-tube with liquid air being used. In the U-tube was found a small amount of solid, with properties resembling those of sulphuryl chloride. The residue was then placed in the apparatus described on page 698 (Figure 2). After passing dry air through the system for an hour, the liquid was distilled into the second flask at 76–78°(23 mm.), when the second flask was sealed off and the distillation conducted at ordinary pressure. It began at 139°, and was chiefly from 149° to 150°. The formation of gas was evident and chlorine was found in the liquid air tube. Sulphuric acid was left in the residue. The distillate became viscous at −128°; a few crystals were visible at −80°, disappearing at −67°.

The study of the crude product of Preparation 13 was to throw more light on the question. This had boiled, in hydrochloric acid, within closer limits, 150–154°, than previous preparations. The latter, owing to presence of much hydrochloric acid or of products of dissociation, had taken the vitreous form on cooling, becoming viscous at a higher temperature without separation of crystals. In this case, however, the viscous liquid became solid with crystals at −110°, which disappeared at −70°.

330 grams of this preparation were distilled at 19 mm., after drawing off most of the excess of hydrochloric acid by exhaustion. 58 grams were collected from 67° to 76°, 177 grams from 75° to 78° and 55 grams were left, largely sulphuric acid, which had probably distilled in the hydrochloric acid current. In the U-tube was much hydrochloric acid; a little chlorine. The first fraction became viscous at −127°, crystallized at −93°, and melted at −54°. The corresponding figures for the second were −134–129°, −87°, and −74°. In both fractions cooling caused no separation of crystals. The second fraction, on redistillation at low pressure, became viscous at −130°, crystallized at −83°, and melted at −72°. There was again no separation on cooling. In the

[61] We prepared a small quantity of sulphuryl chloride by the method of Ruff. This boiled at 69–71° and melted at −58–56°, corr. With water it formed an oil, dissolving quietly. The specific gravity of sulphuryl chloride is given as 1.661 at 21°; the boiling point 75°.

liquid air tube there was still much hydrochloric acid, some chlorine, and a few particles melting at −13°. Two subsequent distillations at low pressure resulted in a product reacting quietly and completely with water, leaving no oil. There was not much decomposition, but evidence of a little sulphuryl chloride. The crystallizing point was −80°, the melting point −70°. This product, distilled in the dry system (Figure 2) boiled at 65° to 69° (14–17 mm.), and, at 768 mm., the first half came over at 137–151°; the second at 151–152°. There was very little residue and very little in the U-tube, chiefly hydrochloric acid. On cooling, no vitreous body separated, but only the crystalline, and at −75°. That there was probably sulphuryl chloride present was shown by a redistillation, from which a portion was obtained boiling from 103° to 141° and melting at −52°. Analysis of the product showed too low chlorine and too high sulphur, as in Preparation 12, and the two preparations were probably similar.

A study of the remainder of Preparation 13, by repeated distillations at very low pressure, showed an increasing tendency to decomposition, and, indeed, more in the direction of equation (1) (page 703). The boiling point was 60° to 64° at 2 to 4 mm. The details need not be considered here, but there was clear evidence of more hydrochloric acid and sulphur trioxide, with less sulphuryl chloride. The amount of chlorine, by analysis, in the main body became less; the sulphur higher.

The deleterious effect of distillation at low pressure was strikingly shown in the treatment of Preparation 14. This crystallized readily without giving the vitreous solid, and melted at −80°, corr. After distillation at 68–70° (15–17 mm.), the product would not crystallize at all, even on inoculation with crystals from another preparation. The specific gravity was 1.782 at 20°, showing the probable presence of sulphur trioxide.

Fractional Crystallization of Chlorsulphonic Acid. — It seems therefore certain that chlorsulphonic acid cannot be purified by distillation, that it is an unstable body, and that even the purest specimens heretofore obtained, including our own, must have been contaminated by the dissociation products.

The boiling point must be always somewhat in doubt. In order to obtain identifying constants which would be less affected by temperature and pressure, e. g., the melting point and specific gravity, we had recourse to fractional crystallization.

200 g. of Preparation 17 became viscous at −132°, crystallized at −100°, and melted at −72°. The entire amount was brought to crystallization and then partly melted. 83 g. of solid were then drawn out of the melted mass by a spirally bent glass rod previously inserted. These

83 g. were then remelted and allowed to partly crystallize, and from the second, half-melted mass 42 g. were taken out. After three more similar fractional crystallizations, 8 g. were finally obtained, which became viscous at —130°, crystallized at —98°, and melted at —72° (—80°, corr.). This product reacted quickly and violently with water, and left no oil.

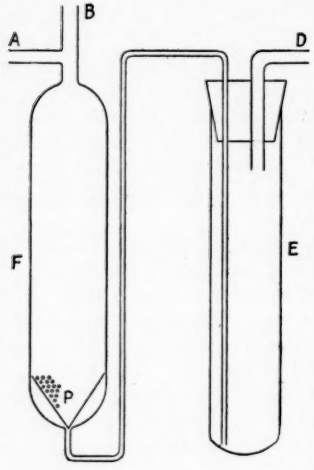

FIGURE 3.

A gravimetric analysis gave: S, 27.66; Cl, 30.32 (Calculated: 27.52 and 30.43). When cooled below —85°, crystallization was not set up by addition of crystals of either sulphuryl chloride or pyrosulphuryl chloride. On stirring or upon addition of crystals of chlorsulphonic acid, the separation was immediate.

Now, as we had satisfied ourselves by experiment that small amounts of both sulphuryl chloride and pyrosulphuryl chloride would alter the melting point appreciably; as both of these substances gave a residual oil with water, even when present in small quantity, and, finally, as the method of preparation precluded even traces of either substance, we could not but conclude that this preparation of chlorsulphonic acid was very pure, and that the true melting point must be in the region of —80°. It remained, therefore, to repeat the fractional crystallization in such a manner that access of moisture to the avid chlorsulphonic acid should be avoided as far as possible.

For this purpose, the apparatus shown in Figure 3 was devised, which consists of the glass separator, F, and test tube, E. The construction is clear from the figure, except that P is a perforated platinum cone fitting snugly into the lower part of F. F, in this case of 50 c. c. capacity, can be placed in a liquid air container. The outlet tubes at A and D are connected with drying tubes of phosphorus pentoxide. Through B may be passed a stirrer. By closing B and applying suction at A, the liquid is drawn from E into F. When the liquid has been partly solidified in F by immersion in the cooler, the residual melted portion is drawn back into a fresh test tube in place of E, while the crystals are held back by the platinum cone. The crystals are then melted in F and drawn into a third test tube at E.

The 261 g. of Preparation 15, which melted at −79°, corr., were introduced into the separator in several portions, and cooled until nearly solid. Crystallization was spontaneous or induced by slight stirring. The crystals were then allowed to half melt, and the residual liquid was drawn out. The remelted crystals, united, were put into the separator a second time and the crystallization repeated. The second crop of crystals was then used for determination of constants.

Melting Point. — Three determinations of melting point by the immersion method (page 699) gave −81°, −81°, and −81.5°, an average of −81.2°, which, corrected, becomes −80.2°. Taking this into consideration with the result of the fractional crystallization of Preparation 17, we may place the melting point of chlorsulphonic acid at −81° to −80°, corr. The purity of the twice crystallized product of Preparation 15 is shown by the slight change in melting point following the treatment.

Specific Gravity.

1. At 20°, 13.4138 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.7533
2. At 20°, 13.4145 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.7536
3. At 0°, 13.6420 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0°}{4°}$ 1.7839
4. At 0°, 13.6410 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0°}{4°}$ 1.7838

(The data above are corrected in order to give the figures for specific gravity: weights of water to 4°, all weights to vacuum.)

The specific gravity of chlorsulphonic acid at 20°, referred to water at 4°, is therefore 1.753; at 0°, referred to water at 4°, 1.784.

Boiling Point. — The boiling point of this sample was compared with that of other preparations. About 60 g. were distilled at 765 mm., corr., with thread of thermometer in the vapor. Ten per cent of the distillate came over at 144–151°, with traces of hydrochloric acid and chlorine. The remainder boiled between 151° and 152°, with no evidence of decomposition in the liquid air tube, which was placed after the receiver. There was a slight residue of sulphuric acid.

Vapor Density. — The determinations of vapor density were made by the method of Victor Meyer at the temperature of boiling aniline (184°). The same precautions were taken as in the case of pyrosulphuryl chloride.

	Substance.	C.c. Air replaced.	T°.	Bar. Corr.	Vapor Density.
1.	0.0522 g.	17.93	19.5	751.1 mm.	2.4
2.	0.0516 g.	18.15	19.5	751.1 mm.	2.4
		Calculated for SO_3HCl			4.04

Analysis. — A gravimetric analysis resulted as follows:

1. 0.9145 g. substance gave 1.1272 g. AgCl
2. 1.2557 g. substance gave 1.5480 g. AgCl
3. 0.5364 g. substance gave 1.0824 g. $BaSO_4$
4. 0.7266 g. substance gave 1.4655 g. $BaSO_4$

	Found.	Calculated for SO_3HCl.
Chlorine:	(1) 30.49, (2) 30.50	30.43
Sulphur:	(3) 27.72, (4) 27.71	27.52

Properties of Mixtures of Pyrosulphuryl Chloride and Chlorsulphonic Acid.

The presence of the two bodies in the product of the Schützenberger reaction and their close relation to each other rendered of interest a comparison of certain properties of their mixtures. As differentiating properties were selected the melting point, boiling point, action with water and with finely powdered tellurium and selenium. The samples of pyrosulphuryl chloride and chlorsulphonic acid used were free from any admixture of the other. The amounts of mixture made up averaged 30 grams. The chlorsulphonic acid gave with tellurium an instantaneous cherry red, persisting for several hours but finally fading. With selenium it gave an immediate moss-green, gradually becoming fainter, then yellow in about an hour, fading in three hours. No colors were obtained with pyrosulphuryl chloride. The table on p. 713 (Table III) gives the results concisely.

From inspection of this table it will be seen that a little over five per cent of chlorsulphonic acid in a mixture of the two bodies would give a color reaction and depress the melting point. Ten per cent would not only give a color reaction, but would cause a considerable lowering of the boiling point and a more immediate action with water. Thirty per cent would give a strong color reaction, a marked action with water, and a marked lowering of the melting point. A chlorsulphonic acid containing thirty-five per cent of pyrosulphuryl chloride would hardly be distinguished from pure material by the color reactions and the action with water, nor would the boiling point suggest much impurity, but the presence of pyrosulphuryl chloride in such a mixture might be inferred from the melting point. It is noteworthy,

TABLE III.

PROPERTIES OF MIXTURES OF THE TWO BODIES.

No.	Percentages.		Melting Point. Immersion Method. Corr. C°.	Boiling Point. Corr. C°.	Action with Water.	Color with Tellurium.	Color with Selenium.
	Pyrosulphuryl Chloride.	Chlorsulphonic Acid.					
1	100	0	−37.5–37	152.5–153	Quiet	None	None
2	99	1	−41–36	151–53	Quiet	None	None
3	95	5	−42–37	143–153	Quiet	Faint pink	Green; then brown to orange yellow
4	91	9	−41–38	142–147	Quiet; dissolves in 10 min.	Strong pink	Yellow brown to orange
5	82	18	−43–39	139–141	Quiet; dissolves rapidly, with heat.	Purple then red	Green then orange
6	70	30	−45–39	139–140	Hissing sound; dissolves at once	Purple then red	Green then orange
7	52	48	−47–43	133–153	Loud hiss; dissolves at once	Purple then red	Green then orange
8	37	63	−50–47	135–153	Explosive	Red	Green
9	25	75	−57–53	139–153	Explosive	Red	Green
10	11	89	−66–61	137–153	Explosive	Red	Green
11	4	96	Pyrosulph. chloride did not separate	142–153	Explosive	Red	Green
12	0	100	−81–80	151–152	Explosive	Cherry red	Green

Except for the color reactions, which were obtained from the components of the mixtures, the properties of Nos. 1 and 12 are of the purest preparations.

also, that the boiling point of a mixture containing 18 to 30 per cent chlorsulphonic acid is within close limits and lower than that of either component.

The Action of Water on Pyrosulphuryl Chloride and Chlorsulphonic Acid and the Separation of the Two Bodies.

Both pyrosulphuryl chloride and chlorsulphonic acid are decomposed by water, the latter far more quickly, according to the equation:

$$(1)\ SO_2OHCl + H_2O = SO_2(OH)_2 + HCl.$$

The formation of chlorine in small quantity from this reaction is evident from the color of the product and its action with potassic iodide. This is probably due to a slight dissociation from the heat of reaction, and a consequent oxidation of the hydrochloric acid by the sulphur trioxide (reactions (1) and (3), pages 703 and 704).

The action of water upon pyrosulphuryl chloride might take place in two ways: either a direct conversion to sulphuric acid and hydrochloric acid according to

$$(2)\ S_2O_5Cl_2 + 3H_2O = 2SO_2(OH)_2 + 2HCl$$

or with intermediate formation of chlorsulphonic acid, according to

$$(3)\ S_2O_5Cl_2 + H_2O = 2SO_2(OH)Cl,$$

the chlorsulphonic acid being then decomposed according to equation (1). The observed formation of chlorine in this reaction also might be ascribed to dissociation of either body under the heat of reaction.

Konovaloff,[33] who added to 100 parts of pyrosulphuryl chloride 4 parts of water (theory for equation (2), 25.1 parts; for (3), 8.4 parts), obtained a mixture of the two bodies. Billitz and Heumann,[47] who used 7.5 parts to 100, found that chlorsulphonic acid was the chief product. Prandtl and Borinski,[49] with the proportion of 100 of substance to 8.3 of water, obtained a product which still reacted quietly with water and gave no color with tellurium, thus showing, according to our results in Table III, at most a small amount of chlorsulphonic acid. They concluded, therefore, that the reaction took place according to equation (3), but was very gradual and, in that instance, incomplete. This opinion would seem to be substantiated by their method of separation of the two bodies, which depends upon the selective attack of water in the form of ice upon the ice-cooled mixture, the chlorsulphonic acid being completely broken down and but little of the pyrosulphuryl chloride.

The question was studied by us in several ways: *a*. Pyrosulphuryl chloride was dissolved in chloroform and one molecule of water added, drop by drop. Hydrochloric acid was given off and a liquid separated which was shown to be sulphuric acid. The chloroform solution was then distilled to expel the solvent. The residue hissed with water, left some oily drops and solidified from −30° to −100°. It was then dissolved in chloroform, and a second molecule of water added as before. Hydrochloric acid was again given off, and sulphuric acid separated. The residue from the chloroform evaporation hissed more violently with water than before, and solidified at −95–100°. A similar treatment with a third molecule of water gave hydrochloric acid in clouds, more sulphuric acid separated, and the chloroform solution yielded a small residue, which still gave the reactions of chlorsulphonic acid and solidified below −80°. The reaction was followed quantitatively, though roughly, and the amount of sulphuric acid was somewhat below that demanded by equation (2).

Evidently in this experiment the reaction has taken place in two stages, represented by equations (3) and (1), the net result being according to equation (2), though the last action was not entirely complete.

b. Pyrosulphuryl chloride was dissolved in carbon tetrachloride, and water was added directly in the proportion of 8.4 to 100 (equation (3)). The mixture was allowed to stand over night. From a portion the solvent was evaporated by a rapid current of dry air; the turbid residue reacted quietly with water. The remainder was evaporated at a gentle heat, and left a residue which also gave no violent action with water. This would seem to show that reaction (3) had not taken place exclusively, but probably reaction (2) incompletely, though, of course, at least 18 per cent of chlorsulphonic acid may have been present according to Table III, 5.

c. Pyrosulphuryl chloride was exposed to the moist air of the room in a beaker covered with a watch glass for seven days, and a portion tested each day with water. There was no evidence of chlorsulphonic acid, — merely a diminishing quantity of pyrosulphuryl chloride, until, on the last day, the residue was sulphuric acid alone. The beaker walls were covered with aqueous hydrochloric acid.

d. 8.3 parts of water were added to 100 parts of pyrosulphuryl chloride, cooled to 0°, and shaken under ice cooling for an hour. The liquid became turbid at first, and a little gas containing chlorine was evolved. In twenty minutes the mixture was decidedly yellow. At the end, two layers were formed, the lower, from its action with water, being apparently unaltered pyrosulphuryl chloride and the upper sul-

phuric acid. The amount of unaltered substance was greater than if only one molecule of water had been added according to equation (2).

e. 8.1 parts of water were added to 100 parts of pyrosulphuryl chloride warmed to blood heat. Hydrochloric acid was given off, and the mixture separated into two layers, sulphuric acid and apparently unchanged pyrosulphuryl chloride, colored by chlorine. The amount unaltered was again greater than would have been expected if somewhat less than one molecule of water (8.1 parts) had acted according to equation (2).

From Experiments *b*, *c*, *d*, and *e* it might be concluded that pyrosulphuryl chloride was directly converted by water to hydrochloric and sulphuric acids, except for the fact that a considerable admixture of chlorsulphonic acid might show no violent action with water (Table III), and that, in Experiments *d* and *e*, the amount of unaltered pyrosulphuryl chloride is greater than it should be if only one third had been converted to hydrochloric and sulphuric acids. Experiment *a*, however, shows that there is an intermediate stage of conversion, — to chlorsulphonic acid. In general, a greater concentration of water will bring about a more complete decomposition of the pyrosulphuryl chloride, after the admixed chlorsulphonic acid has been disposed of, and, in addition, the reaction is furthered by a high temperature or long contact, or by both. If the reaction mixture is at once distilled, the first product, chlorsulphonic acid, may be isolated. This is shown by our investigation of the Prandtl and Borinski method of separation, in which distillations of moist "pyrosulphuryl chloride" obtained by this method gave invariably large amounts of chlorsulphonic acid. One instance will suffice :

f. 133 grams of moist "pyrosulphuryl chloride," which had no longer given any evolution of hydrochloric acid on adding ice, thus showing the chlorsulphonic acid in the original mixture to have been decomposed, were distilled. Up to 148°, 75 g. were obtained; from 148° to 153°, 40 g. Both fractions reacted violently with water and gave a strong red color with tellurium.

We are now in a position to explain why the results of Konovaloff and of Billitz and Heumann differed from those of Prandtl and Borinski. The first three authors apparently distilled their mixture of pyrosulphuryl chloride and water within a short time, and therefore obtained more chlorsulphonic acid, since at the *higher* temperature the pyrosulphuryl chloride was hydrated more quickly and there was not enough water left to entirely decompose the chlorsulphonic acid formed. The last two, however, distinctly state that the cooled mixture stood over night before separation and distillation, hence, at the

lower temperature, the chlorsulphonic acid was more quickly hydrated and therefore not evident in the product of the subsequent distillation.

On this point depends much of the success of the Prandtl and Borinski method, as our study of it shows. If ice be added to a cooled mixture of the two bodies, the chlorsulphonic acid will be decomposed and a part of the pyrosulphuryl chloride. The latter must not be separated at once and distilled, but the mixture must stand for some time. The sulphuric acid does not always form the upper layer, since the specific gravities of the two are so nearly the same. Addition of concentrated sulphuric acid or a little water will bring the pyrosulphuryl chloride to the bottom. After separation, the addition of phosphorus pentoxide to the moist pyrosulphuryl chloride is not optional, as Prandtl and Borinski contend, but necessary, if the minimum amount of chlorsulphonic acid is to be formed on distillation. With proper precautions, the method can be made to give a fairly pure product, though the entire absence of chlorsulphonic acid is not assured. The yield is, however, not over 70 per cent, as Prandtl and Borinski state, and may be less.

In this connection, the behavior of pyrosulphuryl chloride toward concentrated sulphuric acid is of interest. There is no immediate action, but a partial hydration takes place on standing. The two immiscible substances were sealed in a tube and allowed to stand in the cold for a month. The product was homogeneous. On opening the tube there was no excess of pressure; on mixing a portion of the contents with water, a violent reaction took place and hydrochloric acid was given off. This indicates the formation of chlorsulphonic acid. Since we have shown that chlorsulphonic acid is partially dehydrated by sulphur trioxide (p. 673), we may express both results again by writing the reaction (6) in this place also:

$$S_2O_5Cl_2 + H_2SO_4 \leftrightarrows 2SO_3HCl + SO_3,$$

or

$$S_2O_5Cl_2 + 2H_2SO_4 \leftrightarrows 2SO_3HCl + H_2S_2O_7.$$

This condition of equilibrium explains why, in the preparation of chlorsulphonic acid by the Williamson method, the formation of pyrosulphuryl chloride is impossible, since the large amount of sulphuric acid would cause the reaction to run to the right.

Summary.

The work of previous investigators on the action of sulphur trioxide upon certain chlorides is reviewed as briefly as possible and the results summarized in tabular form (Table I).

Pyrosulphuryl chloride is obtained in a perfectly pure state and its chief constants determined. A rapid method is devised for finding melting points at low temperatures.

Chlorsulphonic acid is shown to be unstable when subjected to distillation, but it is purified by crystallization and its chief constants are determined.

It is confirmed that the Schützenberger reaction of sulphur trioxide upon carbon tetrachloride, which is best adapted to the preparation of pyrosulphuryl chloride, gives also chlorsulphonic acid when the sulphur trioxide is in the form of oleum, and it is shown that the proportion of the two bodies in the product depends roughly upon the hydration of the oleum (Table II). It is also shown that, with a hydration corresponding to that of pyrosulphuric acid, $2SO_3 \cdot H_2O$, or greater, only chlorsulphonic acid is formed, and that, while the limit of the formation of chlorsulphonic acid is theoretically at the hydration corresponding to the formula $2SO_3 \cdot 3H_2O$, yet the increasing concentration of the water up to the latter point results in a more rapid decomposition of the chlorsulphonic acid than the theory demands.

A method of separation of the products of the Schützenberger reaction is described, by which the pyrosulphuryl chloride may be completely freed from chlorsulphonic acid, and the latter may also be recovered.

The conditions under which pure chlorsulphonic acid is best prepared by the Williamson method are studied, and it is confirmed that the action of the hydrochloric acid is only upon the sulphur trioxide in the oleum in excess of that corresponding to the formula $SO_3 \cdot H_2O$.

The dissociation of chlorsulphonic acid is studied and discussed.

Properties of mixtures of pyrosulphuryl chloride and chlorsulphonic acid are given (Table III).

The action of water upon pyrosulphuryl chloride is studied.

In conclusion, we desire to express our indebtedness to the C. M. Warren Fund of Harvard University for assistance in defraying the expense of the liquid air used in this investigation.

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